"FABRICATION AND CHARACTERIZATION OF SILICON NANOWIRES"

A thesis Submitted in partial fulfilment of the requirement
For the degree of
Master of Science in physics
By

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CERTIFICATE

This to certify that, the work in the report entitled ***"Fabrication and characterization of Silicon Nanowires"*** by ***Miss Sigma Sai***, in partial fulfillment of Master of Science degree in PHYSICS at the National Institute of Technology, Rourkela; is an authentic work carried out by her under my supervision and guidance. The work is satisfactory to the best my knowledge.

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Date: 04/05/13 **Sigma Sai**

ABSTRACT

In this project work Si nanowires were fabricated on the Si substrate by aqueous method. In this aquoues method Ag is used for electroless chemical etching. The precursors those were taken are $AgNO_3$, HF and H_2O_2. Si nanowires are fabricated at 55°C. The samples were characterized by X-ray diffraction and scanning electron microscope. Result shows morphology of the Si nanowires by scanning electron microscope. X-ray diffraction confirms the phase Si.The XRD analysis confirms the phase of silicon and crystalline nature of silicon .It is found to be single crystalline with plane (1 0 0).The SEM study shows that the particles were uniform and afterwards the non uniformity arises. At 60 second of electroless deposition, the particles shape became anisotropic. Some of the particles have grown vertically. This kind of non uniform pattern can cause a nonuniform distribution of Silicon nanowires. It is confirmed that the morphology of the nanowires also depends on the resistivity of the wafers.The magnified HRTEM image shows the well-resolved lattice spacing of the silicon nanowire, which depicts the crystalline nature of the silicon nanowire.

Keywords: Fabrication ,Silicon, Nanowires, Electro less Chemical Etching.

INTRODUCTION

CHAPTER – 1

1.1 MOTIVATION AND BACKGROUND

In the last years, there is an increasing demand of nanomaterials. Nanomaterials are in the form of nanoparticles, nanowires, nanotubes. The rising demand is because of its properties. Nanowires are also called as quantum wires because of its dimension. Nanowires are of the diameter nanometers range and length in the range of micrometers. Recently, there is an increase in growing interest in the research work on Si nanowires because of its application in many fields like optoelectronics, sensor field, and photovoltaic applications.If Si nanowires can be used properly in photovoltaic cells then it will be more efficient and can help in solving the energy crisis. Transformation of bulk material to ductile material can be done by the creation of dislocation and fostering dislocation motion at high temperatures of about $2/3^{rd}$ of melting point of bulk or phase transformation at high pressure[1]. Understanding the atomic mechanisms and dynamics of a brittle material impacted by an external force is fundamentally important to theoretical and applied physics, such as atomic lattice elastic-plastic response, brittle-ductile (B-D) transition materials toughness, hardness, and fractures. Currently, with the emergence of new directions in flexible dimensionality of electronic devices and forms as well as advancements in single nanowire (NW) electronics, it has become crucial to assess the nanoscale mechanical responses such as elastic-plastic deformation of the most important semiconductor materials, such as Si and SiC [1,2].Theoretical study reveals that recent developments in simulation techniques have opened new approaches for investigating the microscopic origins of complex nanomaterial phenomena. However, some results are contradictive too i.e. brittle-fracture features with small strain were observed by large atomic number molecular dynamics (MD) simulations for Sic NWs[1,3].On a contrary to that large strain elasticity and ductile fractures were achieved. Yet, the important thing is experimental evidence which is mandatory to clarify the true deformation features and mechanisms of the ceramic nanowires. Simultaneous testing and nanoscale imaging makes understanding of atomic scale features of NWs a big challenge. In particular, with respect to the elastic plastic and B-D transitions, the physical picture regarding the atomic scale mechanisms and dynamics of an individual NW remains to be investigated.NWs are commonly utilized as a vibrating beam in NEMS, because of their nature vibrating continuously at or near their resonant frequency.Any small change in the local environment, such

as perturbations in forces, pressure or mass, can be detected by monitoring the corresponding changes in the resonance frequency of the NWs.This technique of nanowire-based NEMS has been successfully applied in atomic force microscopy (AFM) and various kinds of sensors and actuators. There are many semiconductor material systems which would be suitable for fabrication of nanowire field-effect sensors. Quite a few have been demonstrated successfully, including silicon, silicon-germanium, indium oxide, tin oxide, galliumnitride, among others, and yet silicon stands out as a clear favorite for the very same reason that the microprocessors in our computers are crafted from silicon: microfabrication[1,3]. Silicon has proved over and over again to be a practical and versatile material for electronic devices. It does not have the high mobility or direct band-gap of III-V compound semiconductors but it can be grown cheaply, has a stable oxide, has reliable etchants, allows for good control over electronic properties and can be fabricated on scale of very-large wafers. Even in our own lab, we tried several othermaterial systems and growth methods before settling on silicon as our material of choice Advances in the design,synthesis and characterization of nano-materials are expected to provide the unprecedented ability to manipulate matter at the most fundamental level, allowing the implementation of novel nanometer scale devices and systems with unique properties and of utmost technological importance. Bottom-up growth has enabled researchers to demonstrate a myriad of nanostructures of various material compositions and geometries. However, it remains a challenge to turn some of these materials, which are admittedly exciting and beautiful, into robust device technologies. Ultimately, nature seems to favor bottom up organization and thus it is certainly a useful and noble task to pursue. By using top down fabrication, on the other hand, the semiconductor industry has demonstrated the ability to create billions of nanostructures on a single square centimeter of silicon.In the rush to produce exciting end results, the details are lost and ultimately the results are less understandable and less compelling. In the case of bio-sensing, where we must combine aspects of solid-state device physics and electrical engineering with chemistry, biochemistry, and fluid mechanics it is difficult for one individual to be fully versed in all the details. And yet to fully understand and appreciate the complexity of the operation of nanowire sensors, it is important to have a detailed understanding of the solid-state physics, chemistry, and mechanics that combine to produce a measurable effect[4]. To neglect any of these aspects necessarily leads to poor engineering decisions and to poor science. As a result, we have tried to fully understand our nanowires as semiconductor devices prior using them as sensors, and then make use of this understanding to inform the ways in which we use the sensors

in light of what we know about biochemistry and fluid mechanics. The result is hopefully a more complete, robust and usable system for bio-sensing.When the physical dimensions of a device are reduced to the nanometerscale, quantum phenomena become prevalent modifying the optical and electronic properties of the material.Therefore, it is of great scientific interest to characterize the vibrational properties of NWs.

1.2 PROPERTIES OF SILICON BULK

Semiconductor devices are key components in modern electronic systems. Silicon and gallium arsenide with its related III-V compounds form the basis of the most commonly used semiconductor materials. However, silicon is by far the major player in today's electronics market, dominating the microelectronics industry with about 90% of all semiconductor devices sold worldwide being silicon based. Silicon is a semiconductor material with the band gap of 1.12eV. Silicon possesses two of the most outstanding natural dielectrics, silicon dioxide (SiO_2) and silicon nitride (Si_3N_4),which are essential for device formation. In particular, SiO2, which is the basis of the metal–oxide – semiconductor devices (MOS) can be grown thermally on a silicon wafer, it is chemically very stable and can achieve a very high breakdown voltage. The interface defects of the thermally grown $SiO_2$by reaction of oxygen with a silicon wafer are several orders of magnitude lower than those of any deposited film.Silicon is non-toxic, relatively inexpensive (silicon comprises about 26% of the earth's crust which makes it second in abundance only to oxygen), easy to process (a very well established industrial infrastructure in silicon processing exists around the world), and has quite good mechanical properties (strength, hardness, thermal conductivity, etc.).For all the above reasons, silicon is the cornerstone material in electronic systems.However, one of the most vital limitations of bulk silicon is in optoelectronic applications, because of its inefficiency at emitting light[4,5].This is due to its indirect energy bandgap, which generally makes optical transitions in the bulk material at room temperature a very rare phenomenon. In a semiconductor with an indirect fundamental energy bandgap, the maximum of the valence band and the minimum of the conduction band are found at different locations in the k-space, therefore energy required for transition is actually more than the bandgap. Recombination by a single photon – which possesses negligible momentum – is not allowed, because of momentum conservation. Participation of a phonon with the right momentum is necessary to satisfy momentum conservation. Phonons are quantized modes of lattice vibrations that occur in a solid. In the bulk material, this phonon assisted optical transition is very weak, allowing many other non-radiative processes to dominate resulting in a huge drop

in the light emission efficiency. Bulk silicon is therefore not suitable for the fabraication of optoelectronic devices. To date, the semiconductor optoelectronics industry has been dominated by the III-V compound semiconductors, because of their high efficiency in optical transitions primarily due to their direct fundamental energy band-gap. It is an intrinsic semiconductor.It has diamond shaped crystal structure.It is very brittle and has marked metalloid luster. Its atomic number is 14 and atomic mass is 28.08g mol^{-1}. Generally it is tetravalent in its compounds but it can be bivalent sometimes. Its melting point is 1410^{o}C and boiling temperature is 3265^{o}C. Silicon is a refractory material.

1.3 PROPERTIES OF SEMICONDUCTOR NANOWIRES

Nanowires are hair-like, one-dimensional (1D) nanomaterials with diameters in the sub-one hundred nanometer scale and lengths ranging from several hundreds of nmto as high as a few cm. Owing to their nanoscale dimensions in the radial direction, they have size confinement effects that give them novel physical properties ascompared to bulk materials. Their one-dimensional geometry on the nanometerscale provides an extremely high surface area with a nanoscale radius of curvature and great mechanical flexibility with near theoretical strength. These properties areadvantageous in many chemical and mechanical applications. The geometry alsoSi nanowires have greater surface to volume ratio than the Si bulk material. As we go on reducing the size of Si bulk material the number of surface atom increases. As the number of surface atoms increases its optical absorbance also increases. That means optical absorbance of Si nanowires is more than Si bulk material. The optical absorbance of Si nanowire is highest in larger wavelengths. In UV and IR spectrum the reflectance of the Si nanowire is less than 5%. Band gap is a function of the diameter of nanowires. So as the size of the Si bulk material decreases its band gap increases. But the increase in the band gap is very less, in decimals. For example a 3.2 nm diameter Si nanowires has a band gap of 1.50 eV [15, 16, 17].Melting point of the material also depends on the size. As the size of the material reduces the number of surface atoms increases and because of this the atoms have less neighboring atoms. Less neighboring atoms result in less cohesive energy among them. So less heat is required to break the bonds. So melting point of the Si nanowire is less than Si bulk materials.As Si nanowires have greater surface to volume ratio its surface reactivity is more provides anisotropic properties that should be interesting from the point of view ofnanomaterials science and engineering. Their length, reaching as high as the cmscale, makes them easy to manipulate for device fabrication. Nanowires are promising materials for advanced optoelectronics. In addition to the unique

aspects of their physical, chemical, and mechanical properties, the size of these materials is comparable to visible light in wavelength from 400 to 650 nm[18].This implies that nanowires can be used to handle light on a nanometer scale andthus can be used as building blocks for advanced optoelectronics. Indeed, novelmethods of the manipulation of light with nanowires, including nanoscale Fabry–Perrot mode stimulated emission, wave guiding of photons, random lasing action, highly efficient luminescence, and extremely sensitive photo-detection, have recently been demonstrated. The concept of many advanced nanowire-based optoelectronicdevices including light-emitting diodes (LEDs)

1.4 APPLICATIONS OF SILICON NANOWIRES

Optical communications industrial growth has generated a high demand for efficient and low-cost materials to be used for properties and functions such as light emission, detection and modulation. Also, siliconbased materials with enhanced optical properties have applications in accelerating the efficiency of photovoltaic solar cells, which is a market also dominated by silicon, and which is expected to experience a tremendous growth in the near future. The importance of developing a technology that would allow optical and electronic devices to be easily integrated on a silicon wafer has long been recognized. Over the past 15 years, considerable efforts have been carried out within the research community for achieving this goal. Several materials and methods have emerged out to be as possible contenders for silicon-based optoelectronic devices and applications which includes silicon-based superlattices and quantum dots facilitating quantum confinement in silicon nanocrystals [3,4]; SiGe and SiGeC devices doped with optically efficient rare earth impurities such as erbium direct integration of III-V materials on silicon; porous silicon; silicon and carbon clusters embedded in oxide or nitride matrices; superlattices of epitaxially grown silicon with adsorbed oxygen.Most of the above mentioned techniques involve devices that are based on nanoscale silicon.Electrons in the conduction band and holes in the valence band are confined spatially by potential barriers in nanostructures. Where as in quantum dots, carriers are confined in all three dimensions (3D quantum confinement). In a nano-wire, the carriers are confined in two dimensions and are free in only one dimension (2D quantum confinement). In a superlattice, carriers are confined in only one direction and free to move on the plane (1D quantum confinement). Such quantum confined superlattices based on gallium arsenide (GaAs) and indium phosphide (InP) have already found commercial applications in semiconductor distributed feedback lasers (DFB), semiconductor optical amplifiers, and VCSELs for optical communications [14, 15].Basically, in all cases

quantum confinement pushes up the allowed energies effectively increasing the bandgap. The up-shift of the quantum confined bandgap increases as the nanoparticle size becomes smaller. It also increases as the characteristic dimensionality of the quantum confinement increases (from 1D to 2D to 3D). Therefore, quantum confinement may be used to tune the energy of the emitted light in nanoscale optical devices based on the nanoparticle size and shape.Requirement for momentum conservation in the optical transition is one of the vital issues. The bandgap remains indirect in silicon, even for the highest degree of confinement and nanoparticle size of about 3 nm in diameter. In order to facilitate momentum conservation in the radiative transition inclusion of a phonon with the right momentum is required. The light emission in indirect bandgap silicon nanocrystals can be explained in terms of phonon assisted exciton recombination across the bandgap. An exciton is a pair of an electron and a hole bound to each other by Coulomb interaction. The exciton is similiar to a hydrogen atom exceptfor the binding energy of the exciton is much smaller than that of the hydrogen atom. In a defect free crystal, at room temperature, there are two competing processes i.ephonon assisted radiative recombination and the other the process of exciton break-up due to the interaction with phonons which involves phonons and excitons.Which should possesses the right momentum to bridge the separation in momentum space between the top of the valence band and the bottom of the conduction band. However, any phonon can break-up the exciton as long as it has enough energy. In bulk silicon, the exciton binding energy is small, about 15 meV, and thermal phonons with energy kT 26 meV because of quantum confinement. Furthermore, in a nanoparticle the exciton binding energy increases due to the confinement induced overlap of the electron and hole wavefunctions. In a silicon quantum dot of about 3 nm in diameter the exciton binding energy has been calculated to be larger than 160 meV [16], much larger than the binding energy of the excitons in the bulk as well as the energy of the thermal phonons (kT 26 meV). Therefore, in a nanoparticle excitons cannot be broken up by thermal phonons, thereby allowing the exciton enough time to wait for the phonon with the right momentum to participate in the phonon assisted radiative recombination, producing an efficient light emission at room temperature.have enough energy to break-up the exciton to a free electron and a free hole which move away from each other through the continuum of states in the conduction and valence bands. Therefore, exciton break-up dominates and radiative recombination is very less.Continuum of the valence band and conduction band states is modified into a discrete set of energy levels in nanoparticles,

1.5 LIGHT EMISSION FROM NANOSCALE SILICON

Several techniques have been developed for the synthsis of silicon-based nanostructures utilizing quantum confinement for devices with engineered bandgap, increased functionality, and enhanced optical transitions. Porous silicon is amaterial obtained by electrochemically etching silicon in aqueous hydrofluoric acid solutions, consisting of a network of nano meter size silicon crystallites in the form of nano-wires and nano-dots[5,9]. Porous silicon exhibits bright room temperature photoluminescence in the visible region of the spectrum.Several models have been proposed to explain the observed luminescence, including quantum confinement in silicon nanocrystals, luminescence from siloxene ($Si_6O_3H_6$) and other Si-O-Hcompounds, luminescence.Roomtemperature photoluminescence spectra of a typical poroussilicon sample excited by the 457.9 nmline ofan Argon ion laser[8,9].Silicon nanowires have wide range of applications in today's world.It has applications mainly in the field of photovoltaic applications, sensor field and electronics application.Si nanowire have large surface to volume ratio. For this reason Si nanowires are inculcated in the junction region of photovoltaic cell in an array manner. This results in increase in absorption of light which leads to increase in the efficiency of photovoltaic cells. Si nanowire has more sensitivity as it has more surface area. So Si nanowires are used as biological and chemical sensor.It is also applied in the field of electronic, in transistors. It is also used in fabricating small and compact electrical components.

1.6 DIFFERENT TECHNIQUES FOR FABRICATION OF SILICON NANOWIRES

Several other methods for producing silicon nanoparticles have also been explored.One of the limitations of porous silicon is that the material is not very stable chemically, and that the fabrication parameters and interface chemistry cannot be fully controlled. Therefore, research efforts have been concentrated on manufacturing silicon nanoparticles utilizing standard semiconductor processing techniques such as vacuum deposition by Molecular Beam Epitaxy (MBE) or Chemical Vapor Deposition (CVD), which offer much better control in the layer dimensions and the interface quality[5,6].Devices consisting of thin silicon layers sandwiched between layers of oxide, as well as silicon quantum dots embedded in an oxide matrix have been investigated. Silicon superlattices prepared epitaxially under ultra-high vacuum deposition by MBE silicon layers of only 1 – 2 nm thick, separated by adsorbed monolayers of oxygen have

very low interface defects and show quantum confinement characteristics.Devices prepared from these materials showed strong photoluminescence and electroluminescence at room temperature.Mainly there are two approaches to fabricate Si nanowires those are top-down approach and bottom-up approach.In bottom-up approach generation of supersaturation takes place followed by nucleation and that is followed by subsequent growth.In top-down approach breaking of system takes place to get a subsystem. Here the size of the bulk Si material is reduced to nanowires by adopting different methods.

The techniques to fabricate Si nanowires are given as follows:

- Vapor-Liquid-Solid (VLS) mechanism
- Chemical Vapor Deposition (CVD) mechanism
- Molecular Beam Apitaxy mechanism
- Laser Ablation mechanism
- Aqueous mechanism (Electroless chemical etching)

1.6.1 VAPOR-LIQUID-SOLID MECHANISM

Nanowires are a result of anisotropic, 1D crystal growth on a nanometer scale.Therefore, the key issue related to the growth of nanowires is how to induce 1D crystal growth in a controlled manner. Regarding this, many approaches havebeen studied, including the use of the metal-catalyst-assisted vapor–liquid–solid (VLS) mechanism, the vapor–solid (VS) mechanism, and the template-assisted (TA) mechanism. Among these, the VLS mechanism is the most widely used owing to its simplicity and versatility when applied in many semiconductor systems .The VLS mechanism is a 1D crystal growth mechanism that is assisted by a metalcatalyst. It results in the creation of whiskers, rods, and wires. 1D crystal growthwas initially developed nearly 50 years ago in the Si industry and the mechanism was suggested for wider use by Wagner in 1964 . Figure 1.1 shows a schematic of the VLS mechanism. In this mechanism, the metal catalyst forms liquid alloy droplets at a high temperature by adsorbing vapor components. For some reason,e.g., temperature or vapor pressure fluctuation, the alloy is further supersaturated; i.e. it becomes a solution in which the actual concentration of the components is higher than the equilibrium concentration.[2,3] It then drives the precipitation of the component at the liquid–solid interface to achieve minimum free energy of the alloy system.Accordingly, the 1D crystal growth begins, and it continues as long as the vapor components are supplied. Because vapor

(carries solid components),liquid (catalyst alloy), and solid (precipitated one-dimensional structures) phasesare involved, it is known as the VLS mechanism. At a glance, one can know thatthe size and position of the catalyst are related to the diameter and position of the1D structures, as the liquid phase is confined to the area of the precipitated solid phase.In this method a certain metal impurity is essential as a prerequisite for Si nanowire growth. For example Au particles can be taken as impurity [2].Au is deposited in the Si substrate and heated to a temperature; small Au droplets will be formed on the Si substrate. Then that is exposed to a precursor sillane. Si is incorporated in to Au droplets. And as this continues the Si fabrication takes place.

1.6.2 CHEMICAL VAPOR DEPOSITION

This method is a cost effective method. Here for the growth of Si nanowires SiO granules are used as source material. In crucible of a tube furnace SiO granules are taken. To the tube furnace inert gas supply is given. Near about $1350^{o}C$ temperature is given to the furnace. By it Si gets evaporated and flows from hotter end to the cooler part to the substrate and Si nanowires are formed.

1.6.3 MOLECULAR BEAM EPITAXY

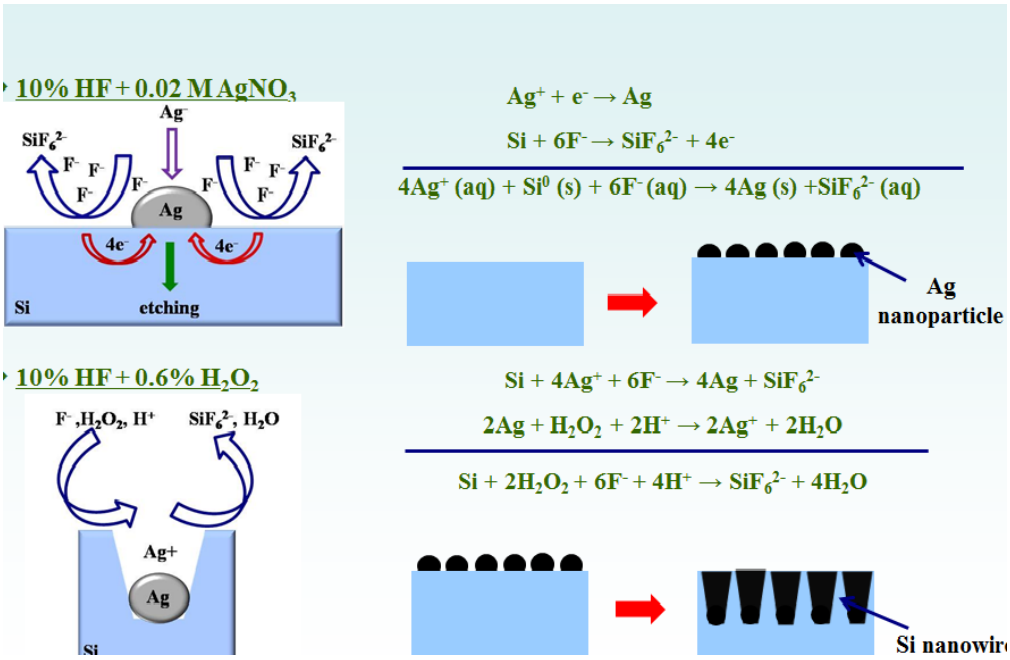
In this method highly pure Si source is taken. Si source is heated till Si evaporates. A gaseous beam of Si atoms that are obtained from the heating is directed towards the substrate to get absorbed and to crystallize. In this way Si nanowires are fabricated. Ultrahigh vacuum is kept in MBE to reduce the contamination.

1.6.4 LASER ABLATION

This is the mechanism by which ultra-thin Si nanowires can be obtained. A pulsed laser is used in this mechanism. A target material is placed in a tube furnace and to it heat is applied. The target material is ablated by using the pulsed laser source. Ablated Si material on it way collides with the inert gas molecules and cools down. As the Si vapor cools it condenses to Si nano droplets. These Si nano droplets falls the substrate to form Si nanowires.

1.6.5 AQUEOUS METHOD (ELRCTROLESS CHEMICAL ETCHING)

Fabrication of nanowires takes place after having several continues reaction in the aqueous solution so it is called as aqueous method. Most commonly for the etching method the elements that are used for deposition are Ag, Au, and Cu on Si substrate. These metals attract the electron from the Si substrate. Oxidation of Si takes place[8,9].In one way to prepare Si nanowires by this method $AgNO_3$/HF solution is taken. Si wafer is dipped in the solution for the deposition. In the solution there are plenty of Ag+ to oxidize Si by take electron from it and also produces SiO_2. In the presence of HF, SiO_2 gets easily etched away. Si under Ag particles are protected. Then by using HNO_3, Ag particles are removed by leaving Si nanowires.



(Fig.1.Formation of Silicon nanowires)

The reactions that are taking place in the solution of AgNO3/HF are as follows:

Ag+ + e-⟶ Ag

$$Si + 2\ H_2O \longrightarrow SiO_2 + 4\ H+ + 4$$

$$e\text{-}SiO_2 + 6\ HF \longrightarrow H_2SiO$$

1.7 OBJECTIVE OF STUDY

The objective of the project work was to focused on the following steps:

1. Fabrication of Si nanowires by aqueous method. Si wafer, $AgNO_3$, HF, H_2O_2 were taken as precursors.

2.Characterization of crystal structure and phase identification of the crystal by XRD.

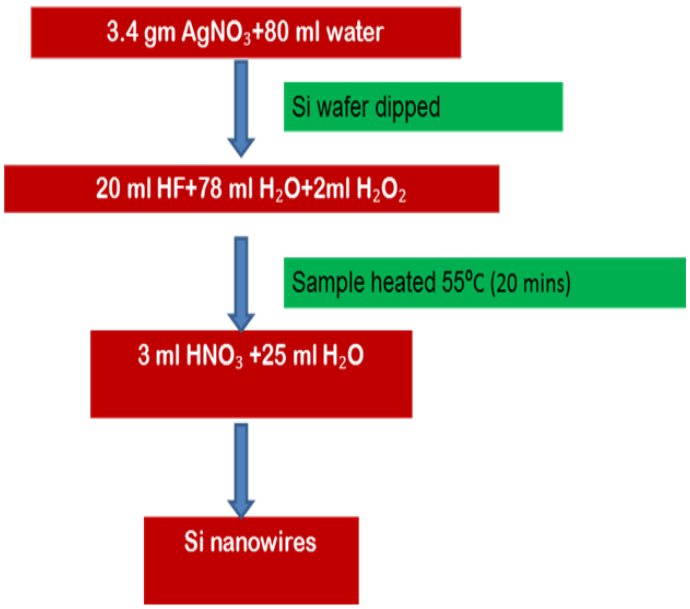
3.Study of morphology by scanning electron microscope.

4.Study of TEM

CHAPTER - 2

2. FABRICATION OF SILICON NANOWIRES

In this project work the fabrication of Si nanowires by aqueous method (electroless chemical etching) is adopted. The materials/chemicals are used here are Si wafer, HF, $AgNO_3$ and H_2O_2. At first the cleaning process is done. The substrate is taken and dipped properly in the deionized water. Then the wafer is cleaned with isopropanol alcohol. After it is cleaned with isopropanol alcohol wafer is again cleaned with 5% of HF. All these cleaning process was done to remove dust, organic ,and other contaminants. After the substrate cleaning was done the glass beakers and the Teflon that were used in the fabrication method were cleaned thoroughly. 3.4 gm of $AgNO_3$ was mixed in 80 ml of water and 20ml of HF was added. Then the Si wafer was dipped in it for 3s and then removed. Same procedure was followed with other Si wafers.



(Fig.2.flowchart and working steps for the fabrication of silicon nanowires is given as above)

A mixture of 20 ml of HF, 78 ml of water was prepared. To this 2ml of H_2O_2 was mixed and kept in a plastic bottle. In a small piece of Si wafers in a Teflon jig and kept inside the bottle. Then the bottle was kept in the oven in 55^0 C. Aqueus solution of 10% of HNO_3 water was prepared. After the sample was removed from the oven it was kept in the prepared HNO3 solution .The shape and morphology of particles are studied by SEM pictures obtained. Whether the particles have attended the nano range is studied by taking the TEM pictures of sample which gives the sharp peaks in XRD analysis.

CHAPTER – 3

3. Characterisation Technique

In order to known the structure, composition, morphology, topography and other various properties of the prepared sample characterization of the sample is necessary. There are many characterization techniques that can give information about the sample. To study the compositional details about the samples generally x-ray diffraction, energy dispersive x-ray spectroscopy, x-ray photoelectron spectroscopy, Auger electron spectroscopy, secondary ion mass spectroscopy, Rutherford back scattering spectroscopy. For the study of morphology of the sample scanning electron microscopy, transmission electron microscopy, atomic force microscopy, scanning tunnelling microscopy are the techniques performed. There are many other techniques also to detect other properties of sample.

In this project work composition and morphology of the samples are detected by using x-ray diffraction techniques and scanning electron microscopy respectively.

3.1 X-RAY DIFFRACTION

This is a technique to study compositional details of the samples. By this technique the average spacing between the atoms, orientation of the single crystal, size and shape of the crystalline are determined.

In materials with a crystalline structure, X-rays scattered by ordered features will be scattered coherently “in-phase” in certain directions meeting the criteria for constructive interference, signal amplification. The conditions required for constructive interference are determined by Braggs’ law.

The relationship describing the angle at which a beam of X-ray particular wavelength diffracts from a crystalline surface was discovered by The English physicist W.H Bragg and is known as Braggs law,

$$n\lambda = 2d \sin\theta$$

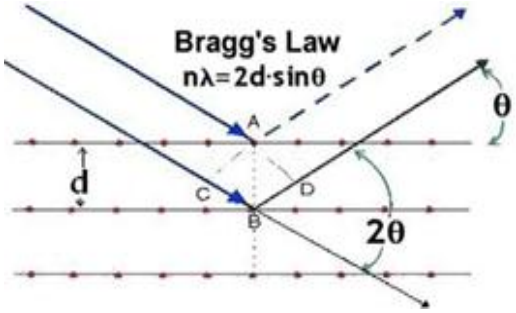


Fig.3.X-ray Diffraction

λ= X-ray wavelength

d = distance between lattice planes

θ= angle of incidence with lattice plane

n = integer

When x-ray passes through the matter it interacts with the atom or electron those are present in it. The distance between the atoms is comparable with wavelength of the x-ray so diffraction takes place. The light deflected from each element will be different and their intensity is also different. When the intensity of those deflected light is plotted with respect to the angle of diffraction peaks are obtained. From these peaks the composition of the material is determined. Size of the crystalline can also be detected from the peak width. If width of the peak increases then the crystalline size of the sample decreases. That means peak width is inversely proportional to crystalline size. Peak width also varies with the angle of deflection 2θ. At larger deflecting angles crystalline size broadening is more.

3.1.1 MATERIAL TYPE FOR XRD

Gas: No structural order – see nothing.

Liquid/Amorphous solids: Order over a few angstroms – broad diffraction peaks

Ordered solids: Extensive structural order – sharp diffraction peaks.

Two types of ordered solids:

1) Single crystals

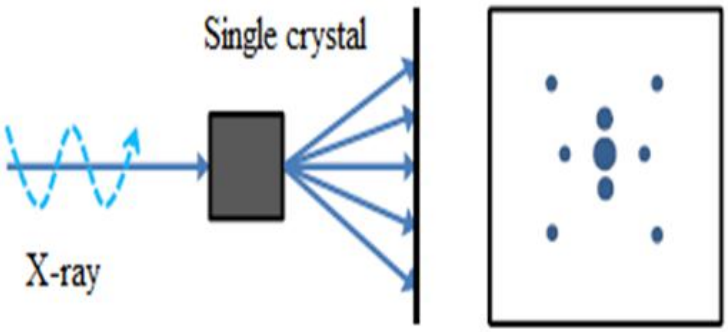
2) Polycrystalline powders

For single crystals large crystals are required. Most common in heterogeneous catalysis and orientationknown. Assume all crystal orientations present. Each lattice plane only present in one orientation. Each lattice plane present at all orientations No overlap of reflections Many overlapping peaks Reflection intensities may be accurately measured. Reflection intensities difficult to determine.

For Single crystals

1. X-rays diffracted from a single crystal produce a series of spots in a sphere around the crystal. (Ewald sphere)

2. Each diffraction peak uniquely resolved



(Fig.4.) X-ray diffraction single of crystal

For Powders

1. All orientations present leads to Continuous 'debye' rings.

2. Linear diffraction pattern with discrete "reflections" obtained by scanning through arc that intersects each debye cone at a single point.

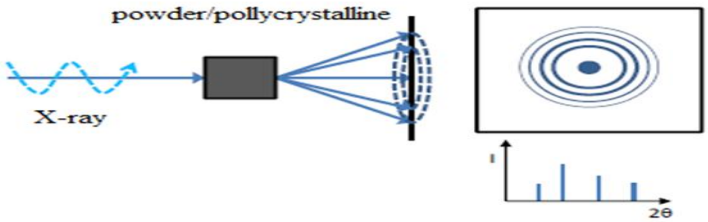


Fig.5.Xrd of Polycrystalline

3.2 SCANNING ELECTRON MICROSCOPY

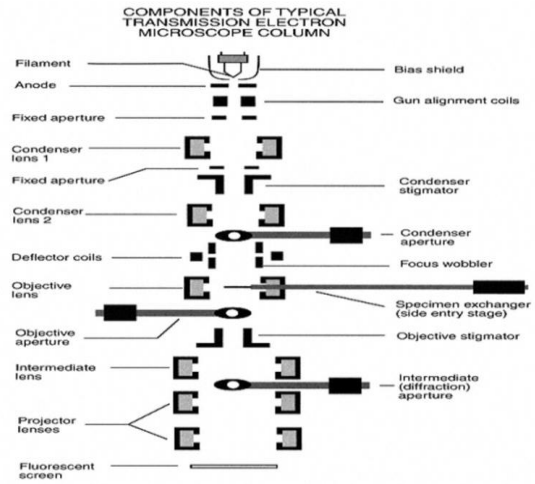
The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample.

In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). The SEM is also capable of performing analyses of selected

point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions (using EDS), crystalline structure, and crystal orientations (using EBSD)[21,23]. The design and function of the SEM is very similar to the EPMA and considerable overlap in capabilities exists between the two instruments.

3.3 Transmission Electron Microscope (TEM)

Electron Microscopes are scientific instruments that use a beam of highly energetic electrons to examine objects on a very fine scale. This examination can yield the information like topography, morphology, composition as well as crystallographic information's. Working principle is exactly as their optical counterparts except that they use a focused beam of electrons instead of light to "image" the specimen and gain information as to its structure and composition. The main use of this technique is to examine the specimen structure, composition or properties in sub-microscopic details so that this microscopy technique is significantly involved in numerous fields. In TEM there is no change in the refractive index of the medium when the illumination beam is deflected, the vacuum in the lens is the same as the vacuum in the column. Deflection is in this case only due to the electromagnetic properties of the lens which are defined by electromagnetic plates that are only able to influence the path direction of the electrons, since all of the electrons carry a negative charge[22].



(Fig.6.Schematic diagram of transmission electron microscopy)

Those electrons that pass through the sample go on to form the image while those that are stopped or deflected by dense atoms in the specimen are subtracted from the image.

In this way a black and white image is formed. Remaining other electrons which passes close to heavy atom and get only slightly deflected make their way down the column and contribute to the image.There are three main reasons why the microscope column must be operated under very high vacuum. The first of these is to avoid collisions between electrons of the beam and stray molecules. Such collisions can result in a spreading or diffusing of the beam or more seriously can result in volatization event if the molecule is organic in nature. Such volatizations can severely contaminate the microscope column especially in finely machined regions such as apertures and pole pieces that will serve to degrade the image quality.

Chapter – 4

4. RESULTS AND DISCUSSION

1) SCANNING ELECTRON MICROSCOPY(SEM)

Silver (Ag) particles were deposited prior to the fabrication of silicon nanowires. The resistivity of the (100) silicon substrate was 1-10 ohm.cm. The thickness of the substrates was ~ 500 μm. The shapes of the Ag particles were varied with electroless deposition time as shown in the figure. At the initial stage the particles were uniform and afterwards the nonuniformity arised. At 60 second of electroless deposition, the particles shape became anisotropic. Some of the particles have grown vertically. This kind of non uniform pattern can cause a nonuniform distribution of Silicon nanowires. Therefore, the particles grown for less time are comparatively uniform and suitable for Silicon nanowires growth. In this study,

1. Fabrication of Silicon nanowires

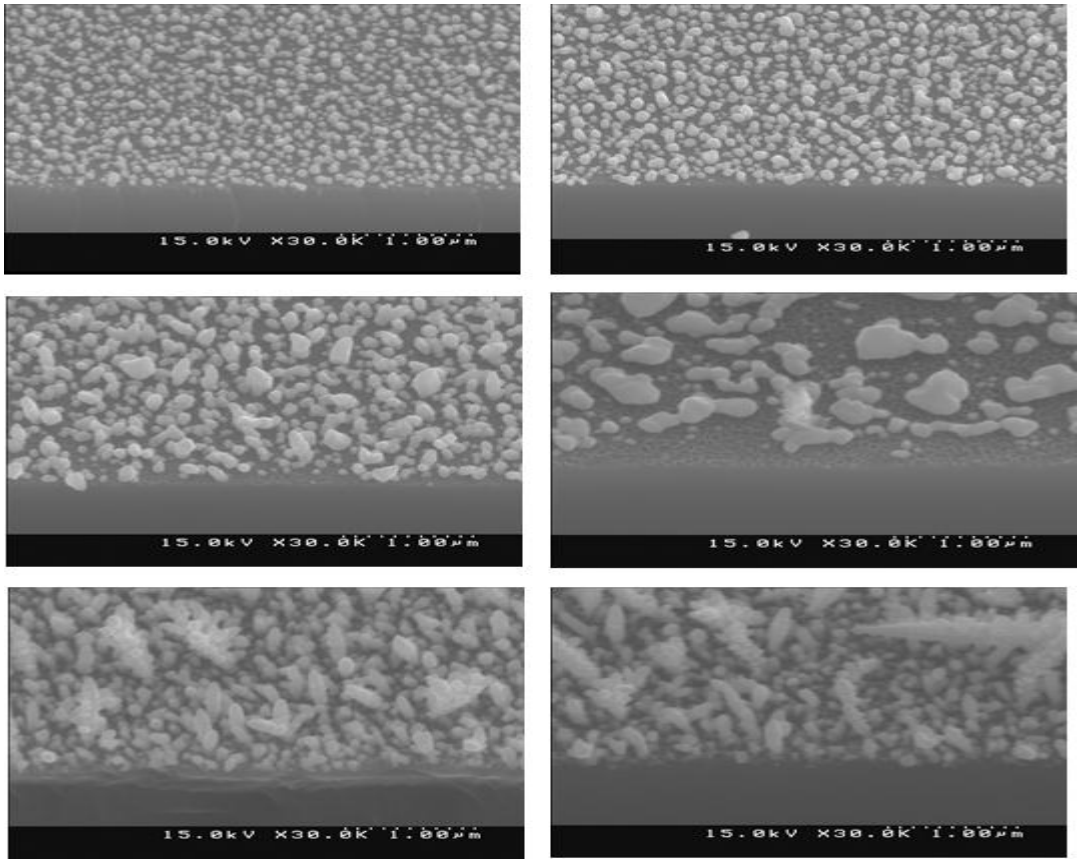


Fig. 7.SEM Images of silver particles grown on silicon substrate (a) 2 s, (b) 5 s, (c) 15 s, (d) 30 s, (e) 45 s and (e) 60 s.

A growth time of 2s is preferred, where the average particle sizes were around 50-120 nm. **Fabrication of silicon nanowires**:The silver particle present on the silicon substrate (1-10 ohm.cm) locally oxydizes the silicon surface by electronic transport. During the HF treatment, the locally oxidized surface etched away to produce local pits. With the increase in etching time the depth of the pit increases. As a result, the smooth surface of the parent silicon wafer becomes nonuniform. As the Ag nanoparticles were very close to each other, the distance between the pits also in nanometer range. Therefore, the non-etched area stands vertically and can be considered as nanowires. The nanowire length depends on the etching time. The nanowires length increases with increase in etching time. The width of the nanowires were around 100-200 nm and length was around 20 μm for an etching of 20 mins. The aspect ratio of the nanowires was more than 100. However, the diameter of the nanowires was not uniform, which may be due to the nonuniform diameter of the silver particles.

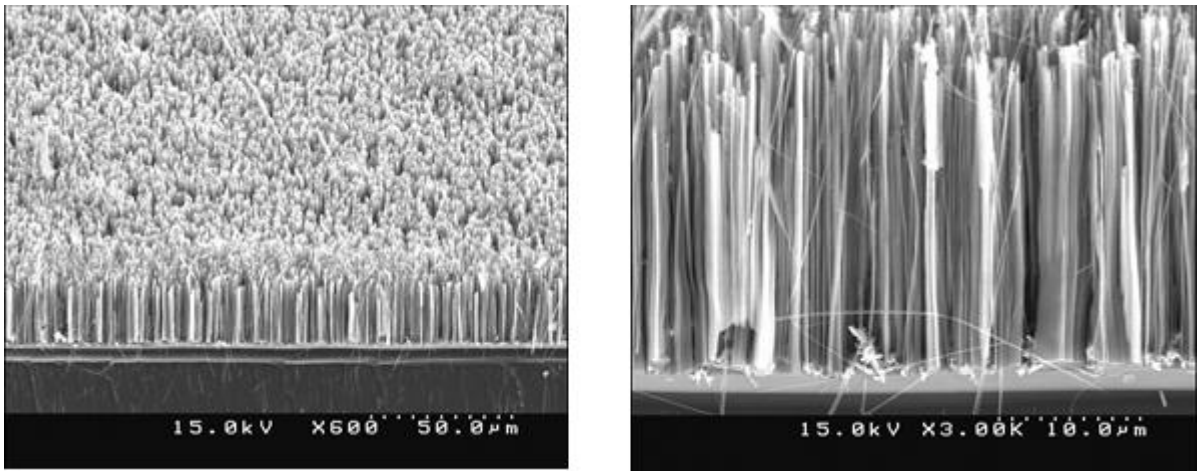


Fig.8. SEM Images of Silicon nanowires at (a) 600 and 3000 magnification

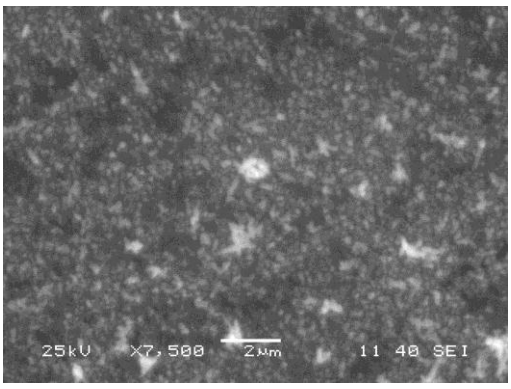
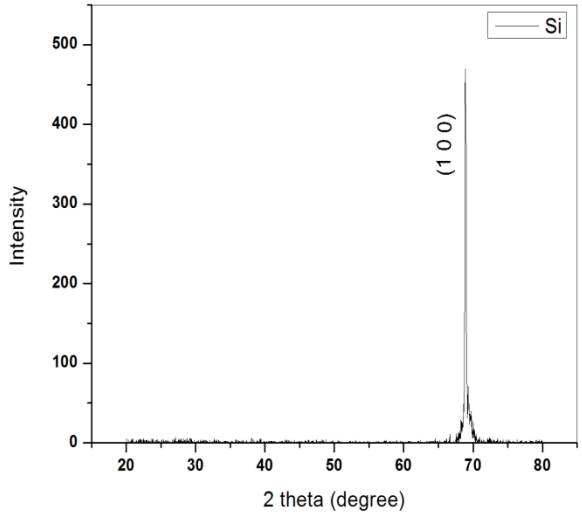


Fig.9. SEM Images of Silicon nanowires at 7500 magnification

The above process is repeated for heavily born doped silicon substrate (resistivity ~ 0.001 ohm.cm), where no formation of the nanowires were found. It is confirmed that the the morphology of the nanowires also depends on the resistivity of the wafers.

X-Ray Diffraction: From the figure the XRD patterns taken by the XRD machine model number (Pan analytical, Xpert Pro) are matched with the JCPDS File and recognized as Silicon.The XRD analysis confirms the phase of silicon and its crystallinity.It is found to be single crystalline with plane (1 0 0).



(Fig.10. XRD result of silicon)

2) TRANSMISSION ELECTRON MICROSCOPY(TEM)

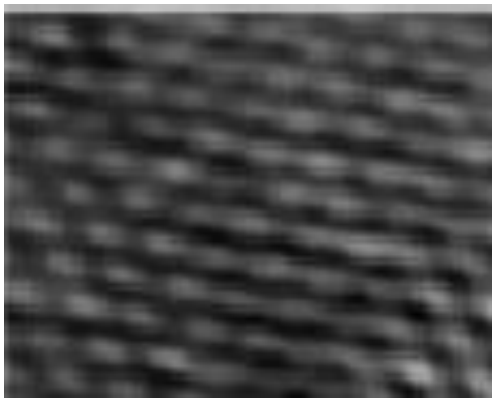


Fig.11.HRTEM image of Silicon nanowires

The HRTEM image of Silicon nanowires is shown in the figure 11. The magnified HRTEM image clearly shows the well-resolved lattice spacing of the silicon nanowire, which depicts the crystalline nature of the silicon nanowire**.**

Chapter-5

5.1 CONCLUSION

Si nanowires were fabricated on the Si substrate by aqueous method. In this aqueous method Ag is used for electroless chemical etching. The precursors those were taken are $AgNO_3$, HF and H_2O_2. Si nanowires are fabricated at 55°C. The samples were characterized by X-ray diffraction and scanning electron microscope.The XRD analysis confirms the phase of silicon and crystallinity nature of silicon. It is found to be single crystalline with plane (1 0 0).The SEM study shows that the particles were uniform and afterwards the non-uniformity arises. At 60 second of electroless deposition, the particles shape became anisotropic. Some of the particles have grown vertically. This kind of non-uniform pattern can cause a nonuniform distribution of Silicon nanowires.It is confirmed that the morphology of the nanowires also depends on the resistivity of the wafers.The magnified HRTEM image shows the well-resolved lattice spacing of the silicon nanowire, which depicts the crystalline nature of the silicon nanowire.

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